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(54) POLYURETHANE PRESSURE-SENSITIVE ADHESIVES

(71) We, THE DUNLOP COMPANY LIMITED, a British Company of Dunlop House, Ryder Street, St. James's, London, S.W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to pressure-sensitive adhesives and to methods of making them.

The invention is a modification of our Patent Application No. 38127/64 (Serial No. 1,113,925). In our Specification No. 38127/64 (Serial No. 1,113,925) there is described and claimed a pressure-sensitive adhesive composition comprising a cross-linked reaction product of one or more polyols having at least three hydroxyl groups per molecule with or without one or more diols and/or one or mono-ols, and an organic polyisocyanate, said reaction product having an average chain-length of from 130 to 285 chain atoms.

We have now discovered that satisfactory pressure-sensitive adhesives having a lower thermoplasticity may be made in which the reaction product has an average chain-length of gerater than 285. Accordingly, in one aspect of the present invention there is provided a pressure-sensitive adhesive comprising a cross-linked reaction product of one or more polyols having at least three hydroxyl groups per molecule with or without one or more diols and/or one or more mono-ols, and an organic polyisocyanate, said reaction product having an average chain-length of greater than 285 chain atoms.

Specification No. 38127/64 (Serial No. 1,113,925) also describes and claims a method of making a pressure-sensitive adhesive comprising reacting one or more polyols having at least three hydroxyl groups per molecule with or without one or more diols and/or one or more mono-ols, and the stoichiometric amount of an organic polyisocyanate, the hydroxyl-containing compounds being in sufficient proportions dependent on their molecular weights to produce a cross-linked reaction product with said polyisocyanate, said reaction product having an average chain-length of from 130 to 285 chain-atoms. Now in a further aspect of the present invention there is provided a method of making a pressure-sensitive adhesive using the method described in 38127/64 (Serial No. 1,113,925) except that the reactants are chosen to give a reaction product having an average chain-length of greater than 285 chain atoms.

The stoichiometric amount of an organic polyisocyanate is the amount of said polyisocyanate required to react with all the hydroxyl groups of the polyols, diols and mono-ols in order to produce a cross-linked reaction product.

The term "chain-length" is used in this Specifiaction to refer to the length of a chain in terms of chain atoms as measured from the point of atachment of a chain branching therefrom, to an adjacent point of attachment of a further branching from the first-mentioned chain, or as measured from the point of attachment of a chain branching from the first-mentioned chain to the end of the first-mentioned chain if the first-mentioned chain is free from attachments at one end. The term "chain-atoms" refers only to the atoms in the main chain and does not include branch-chain atoms.

Preferably, the reactants are applied in a fluid state to a substrate such as a paper or cloth fabric or a thin plastic sheet, whereon they react to form a pressure sensitive adhesive composition, but if desired the reacted adhesives may be used in solvents.

By a "pressure-sensitive adhesive composition" as used in this Specification is

meant a composition which remains tacky over a wide range of temperatures, viz. at least −20°C. to 70°C., and which will adhere to most surfaces when light pressure is applied at ambient temperatures in the absence of heat, moisture and other agents.

The polyols employed in this invention may be hexols, e.g. sorbital; pentols, e.g., arabitol; tetrols, e.g. pentaerythritol; or triols, e.g. glycerol. Also, copolymers of these polyols and propylene oxide and/or ethylene oxide may be used in place of the unmodified polyols. Examples of diols which can be employed are poly(ethylene glycol) and poly(propylene glycol). Examples of mono-ols which can be used are methyl oxitol and n-butanol.

Various combinations of hydroxyl-containing compounds, i.e. mono-ols, diols, triols, etc., can be employed in this invention, for instance, a single kind of tetrol or triol, mixtures of different tetrols and/or triols having difierent molecular weights, mixtures of one or more kinds of diol, and mixtures of one or more kinds of tetrol and/or triol and one or more kinds of mono-ol.

When a diol and triol are reacted with a polyisocyanate in the absence of any other triol or diol and mono-ol, the diol may have a molecular weight of from 1000 to 3000 and triol may have a molecule weight of from 100 to 500.

However, no matter what combination of hydroxyl-containing compounds is used, the amounts used should be such that when reacted with an organic polyisocyanate the average chain length of the reaction product will be greater than 285. For example, when a single triol of the glycerol/propylene oxide copolymer is used, it should have a molecular weight, for example, of the order of from 4000 to 8000 particularly 5000 when reacted with a low molecular weight polyisocyanate. This molecular weight value will be lower if the triol is reacted with a high molecular weight polyisocyanate.

The average reaction product chain-length in terms of the number of atoms in the chain, which a particular polyol and a particular polyisocyanate will produce, is determined by the following method. As an example, a copolymer of glycerol and propylene oxide having a molecular weight of 8000 is reacted with the stoichiometric amount of a commercially available polyether extended di-isocanate-talylene di-isocyanate extended with propylene oxide units to a molecular weight of 850. The average aggregate atomic weight of each arm of the triol is taken as $\frac{8000}{3}$, i.e. 2666. Each arm of the triol is taken as consisting of propylene oxide units (—$CH(CH_3)$—CH_2—O—) and each unit has an aggregate atomic weight of 58 which is taken as being equivalent to only three atoms viz. the chain-atoms, —C—C—O—. Therefore, the number of chain-atoms in each arm of a triol unit in the reaction product is $2666 \times \frac{3}{58}$ i.e. 138.

Taking the molecular weight of the tolylene diisocyanate portion of the polyether extended di-isocyanate as 350 (i.e. two molecules of tolylene di-isocyanate), then the propylene oxide polyether portion must be of molecular weight 500. By a similar calculation to that used for the triol, the chain length of the propylene oxide polyether portion of the extended di-isocyanate is therefore $\frac{500 \times 3}{58}$ i.e. 26 chain atoms. The number of chain atoms in a single toluene diisocyanate molecule is 7, taking the benzene ring as equivalent to three chain atoms. The total chain length of the polyether extended di-isocyanate is therefore 7+26+7=40 chain atoms. Thus, each chain length in the reaction product will have an average number of chain atoms equal to 138+40+138, i.e. 316. This method can be used in reverse to determine which polyol/polyisocyanate mixtures will produce a reaction product having an average chain length of greater than 285 chain atoms.

When a mixture comprising at least one triol and at least one diol is used, the proportions which would theoretically give a poor pressure-sensitive adhesive composition, that is, one which is too hard, may in practice give a reaction product which exhibits good pressure-sensitive adhesive properties. This is owing to the existence of a variation in chain lengths in the reaction product. Thus, a high proportion of chain lengths having an average of greater than 285 chain atoms may be produced from mixtures whose proportions would not be expected to produce a good pressure-sensitive adhesive composition if the resultant product were ideal. By "ideal" is meant that all chain lengths in the reaction product are the same.

The organic polyisocyanate used in this invention may be aliphatic or aromatic, e.g. 4,4¹-diisocyanato-diphenylmethane, tolylene diisocyanates, hexamethylene diisocyanate, triphenylmethanetriisocyanate, 2,4,4¹-triisocyanatodiphenylether and polymethylene polyphenyl isocyanate.

Usually, an accelerator such as dibutyl tin dilaurate or stannous octoate is added to the reaction mixture prior to curing.

Also, if desired, an antioxidant can be incorporated into the reaction mixture prior to curing. This has the effect of stabilising the adhesive composition against changes during ageing.

The present-sensitive adhesive compositions of this invention are advantageous in that they do not need to be dissolved or dispersed in a solvent or dispersing agent, respectively, for application of the composition to a substrate (although they may be used in this manner if so desired), and the degree of tackiness and non-transferability of the composition do not change appreciably over a wide range of temperatures, viz.— 20°C. to 120°C.

The invention is illustrated in tthe following Example which describes the preparation of a pressure-sensitive adhesive having an average chain length of 316 chain atoms.

EXAMPLE

Stoichiometric amounts of a commercially available triol of molecular weight 8000 (10 parts by weight) and of a commercially available polyether-extended tolylene di-isocyanate of molecular weight 850 (1.6 parts by weight) were reacted together in the absence of moisture for two hours at 70°C. using 0.1% dibutyl tin-laurate as accelerator.

The triol was a copolymer of glycerol and propylene oxide and the di-isocyanate was extended with propylene oxide units.

A pressure-sensitive adhesive polymer of low thermoplasticity was produced.

Reference is made to U.K. Patent Application No. 22624/67 (Serial No. 1,216,673) which also relates to the making of pressure-sensitive adhesives.

WHAT WE CLAIM IS:—

1. A pressure-sensitive adhesive composition comprising a cross-linked reaction product of one or more polyols having at least three hydroxyl groups per molecule with or without one or more diols and/or one or more mono-ols, and an organic polyisocyanate, said reaction product having an average chain length of greater than 285 chain-atoms.

2. A composition according to claim 1 including an antioxidant.

3. A method of preparing a pressure-sensitive adhesive composition which comprises reacting one or more polyols having at least three hydroxyl groups per molecule with or without one or more diols and/or one or more mono-ols, and the stoichiometric amount of an organic polyisocyanate, the hydroxyl-containing compounds being in sufficient proportions dependent on their molecular weights to produce a cross-linked reaction product with said polyisocyanate, said reaction product having an average chain-length greater than 285 chain-atoms.

4. A method according to claim 3 wherein one or more triols are reacted with a polyisocyanate in the absence of any other polyol, diol and mono-ol.

5. A method according to claim 3 wherein a triol and a mono-ol are reacted with a polyisocyanate in the absence of any other polyol and diol.

6. A method according to claim 5 wherein the mono-ol is methyl oxitol.

7. A method according to claim 4, 5 or 6 wherein the triol is a copolymer of glycerol and propylene oxide having a molecular weight of from 4000 to 8000.

8. A method according to claim 7 wherein the molecular weight of the triol is 5000.

9. A method according to claim 3 wherein a triol and a diol are reacted with a polyisocyanate in the absence of any other triol or diol and mono-ol.

10. A method according to claim 9 wherein the triol has a molecular weight of from 100 to 500 and the diol has a molecular weight of from 1000 to 3000.

11. A method according to claim 9 or 10 wherein the triol is a copolymer of glycerol and propylene oxide.

12. A method according to claim 9, 10 or 11 wherein the diol is poly(propylene glycol).

13. A method according to any of claims 3 to 12 wherein the polyisocyanate is a dissocyanate.

14. A method according to claim 13 wherein the diisocyanate is 4,4¹-diisocyanatodiphenylmethane.

15. A method according any of claims 3 to 14 wherein an antioxidant is incorporated in the reaction mixture.

16. A method according to any of claims 3 to 15 wherein an accelerator is incorporated in the reaction mixture.

17. A method according to claim 16 wherein the accelerator is dibutyl tin dilaurate.

18. A method according to any of claims 3 to 17 wherein the reactants are applied in a fluid state to a substrate whereon they react to form the pressure-sensitive adhesive composition.

19. A method of preparing a pressure-sensitive adhesive composition substantially as described in the foregoing Example.

20. A pressure-sensitive adhesive composition prepared by the method claimed in any of claims 3 to 19.

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